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Solvent Effect of Methanol on the Rate of Formation Reaction of Monochloroiron(III) Complex in Aqueous Solution

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The rate constants of the formation reaction of $FeCl^{2+}$ complex from Fe(III) and Cl^- ion were measured in water–methanol mixed solvents by use of a stopped-flow spectrophotometer. The apparent rate constant k is dependent upon the acid concentration of the medium, indicating that the reaction can proceed through two parallel paths, $Fe^{3+}+Cl^-$ (k_1) and $Fe(OH)^{2+}+Cl^-$ (k_H). Both k_1 and k_H increase with the increase in the mole fraction of methanol in the medium, x_M. Since k_H is much larger and is consequently much more accurately determined than k_1, considerations were mainly made on the nature of k_H. According to the dependence of k_H on the dielectric constant of the medium, it was found that the activation free energy of the $Fe(OH)^{2+}+Cl^-$ reaction consists of the electrical and non-electrical parts and that the dimension of the activated complex corresponds approximately to the distance of the outer-sphere approach between the reacting species. These facts are therefore in favor of an outer-sphere mechanism in the anation reactions of iron(III) by simple anions.

Many investigations have been done on the kinetics of fast formation reactions of transition metal complexes with various anions since the introduction of the flow method into the field of kinetic measurements;[1] in particular, the reaction of iron(III) with chloride ion, $Fe(III)+Cl^- \rightarrow Fe(III)Cl$, in aqueous solution was one of the earliest studied among the formation reactions of iron(III) complexes.[2]

The reaction is known to be dependent upon acid concentration and to proceed through two parallel steps of $Fe^{3+}+Cl^-$ and $FeOH^{2+}+Cl^-$, the latter being much faster than the former. Since the reaction occurs between ions of opposite signs, it may be supposed to be affected by the change of dielectric constant of the solvent. In order to prove this effect, mixed solvents of methanol and water were adopted; the reaction mechanism has been discussed in the present research.

Experimental

Materials. Iron(III) perchlorate was prepared by dissolving pure iron wire in perchloric acid, followed by oxidation with hydrogen peroxide. Methanol was purified by ordinary distillation of commercial methanol of S. P. grade under atmospheric pressure. Sodium chloride and sodium perchlorate were twice recrystallized from aqueous solution.

Determinations of Equilibrium Constants. The hydrolysis constant of Fe^{3+}, $K_H=[FeOH^{2+}][H^+]/[Fe^{3+}]$, the association constant between Fe^{3+} and ClO_4^-, $K_a=[Fe^{3+}\cdot ClO_4^-]/[Fe^{3+}][ClO_4^-]$, and the formation constant of $FeCl^{2+}$ complex, $K_1=[FeCl^{2+}]/[Fe^{3+}][Cl^-]$ at various mole fractions of methanol, x_M, were determined spectrophotometrically by use of a Hitachi-Perkin-Elmer UV-VIS spectrophotometer Model 139. The ionic strength of the solutions was adjusted with sodium perchlorate.

Kinetic Measurements. The measurements of the rate constants were performed by use of a Yanagimoto stopped-flow spectrophotometer SPS-1. Since the strict regulation of the reaction temperature was impossible in the present apparatus, the rate constants at desired temperatures were obtained by a graphical interpolation from those measured at temperatures close to the desired. The signals drawn on the memoriscope were photographed and analyzed.

Results and Discussion

Hydrolysis Constants of Fe^{3+}. When some of Fe^{3+}_{aq} is hydrolyzed to give $Fe(OH)^{2+}$ in slightly acid solution, the following relationship holds at total iron(III) concentration [Fe(III)]:

$$\frac{[Fe(III)]}{A_H}=\frac{1}{\varepsilon_H}+\frac{[H^+]}{\varepsilon_H K_H} \tag{1}$$

where A_H and ε_H represent the optical absorbance due to $Fe(OH)^{2+}$ ($A_H=\varepsilon_H[FeOH^{2+}]$), and the molar absorptivity of $Fe(OH)^{2+}$, respectively. From a linear relationship of $[Fe(III)]/A_H$ *vs.* $[H^+]$, ε_H and K_H can be obtained. At first, since A_H is not known yet, the total absorbance A and the total acid concentration $[HClO_4]$ are used in place of A_H and $[H^+]$ in Eq. (1), respectively. From the rough linearity, an approximate K_H is obtained, and therefore an approximate $[H^+]$ and A_H. The method of successive approximations gives the final value of K_H. The observation was performed at $[Fe(III)]=2\times10^{-4}$ M, $[HClO_4]=4\times10^{-3}$—9×10^{-3} M, $\mu=0.5$ M, 25 °C, and wavelength 350 nm. A typical case of the linear relationship of Eq. (1) at $x_M=0.395$ is shown in Fig. 1 and the values of K_H at various methanol concentrations are listed in Table 1, among which those for $x_M=0.15$—0.25 are

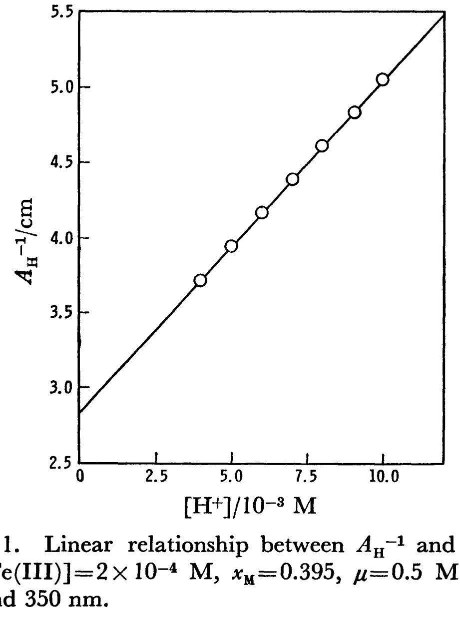

Fig. 1. Linear relationship between A_H^{-1} and $[H^+]$ at $[Fe(III)]=2\times10^{-4}$ M, $x_M=0.395$, $\mu=0.5$ M, 25 °C, and 350 nm.

reproduced from our previous literature.[3]

There exists the apparent feature that K_H increases with increasing methanol concentration; this is reasonable in view of the decrease in dielectric constant of the mixed solvent as the methanol concentration increases.

Ionic Association Between Fe^{3+} *and* ClO_4^-. When the perchloric acid concentration is relatively high in the mixed solvent, the phenomenon of ion-pair formation between Fe^{3+} and ClO_4^- ions has to be taken into account in the course of determination of the formation constant K_1, as will be described in the next section.[3]

The apparent molar absorptivity of the solution containing Fe^{3+} and perchloric acid, ε, may be expressed as follows:

$$\varepsilon = \frac{\varepsilon_0 + \varepsilon_H K_H/[H^+] + \varepsilon_a K_a[ClO_4^-]}{1 + K_H/[H^+] + K_a[ClO_4^-]} \qquad (2)$$

where ε_0 and ε_a represent the molar absorptivity of Fe^{3+}_{aq} ion and the ion-pair $Fe^{3+}\cdot ClO_4^-$, respectively. Since K_a is very small, $K_a[ClO_4^-]$ is negligible compared to unity. When the acidity of the solution is high enough, $[FeOH^{2+}]$ may be negligibly small and, therefore, Eq. (2) is reduced to the following simple expression at a suitable wavelength:

$$\varepsilon = \varepsilon_0 + \varepsilon_a K_a[HClO_4] \qquad (3)$$

The observations were performed at $[Fe(III)] = 1.0\times10^{-2}$ or 2.0×10^{-2} M and $[HClO_4] = 2.40—3.60$ M at a wavelength of 350 nm. The linear relationships of ε against $[HClO_4]$ are shown in Fig. 2, from whose slopes $\varepsilon_a K_a$ are obtained as listed in Table 1 at various x_M's. The values of $\varepsilon_a K_a$ will be necessary in the calculation of K_1.

Formation Constants of $FeCl^{2+}$. When Cl^- ion is added to the mixed solution containing iron(III) and perchloric acid, there occurs an additional complex formation between iron(III) and Cl^- ion. If the species of the complex formed is only $FeCl^{2+}$, Eq. (2) can be modified as follows:

Table 1. Hydrolysis constant, K_H, formation constant of $FeCl^{2+}$, K_1, and constant of ionic association for $Fe^{3+}\cdot ClO_4^-$, $\varepsilon_a K_a$, at different methanol concentrations, x_M, at 25 °C

x_M	K_H M	$\varepsilon_a K_a$ $M^{-2}cm^{-1}$	K_1 M^{-1}
0	1.65×10^{-3}	—	4.0
0.15	4.8×10^{-3}	3.33	2.6×10
0.20	6.2×10^{-3}	5.56	4.3×10
0.25	8.7×10^{-3}	7.06	5.0×10
0.395	1.38×10^{-2}	10.94	1.13×10^2
0.443	1.56×10^{-2}	12.57	1.37×10^2
0.519	1.90×10^{-2}	12.50	1.44×10^2

$$\varepsilon = \frac{\varepsilon_0 + \varepsilon_H K_H/[H^+] + \varepsilon_a K_a[ClO_4^-] + \varepsilon_1 K_1[Cl^-]}{1 + K_H/[H^+] + K_a[ClO_4^-] + K_1[Cl^-]}$$

where ε_1 is the molar absorptivity of $FeCl^{2+}$.

By adopting reasonable approximations, as has been done above, the following equation can be derived at $[HClO_4] = 3.0$ M:

$$\varepsilon = \varepsilon_1 - \frac{\varepsilon - \varepsilon_0 - \varepsilon_a K_a[HClO_4]}{K_1[Cl^-]} \qquad (4)$$

The linear relationship between ε and $(\varepsilon-\varepsilon_0-\varepsilon_a K_a[HClO_4])/[Cl^-]$ was proved at $[Fe(III)] = (1-2)\times10^{-3}$ M, $[NaCl] = (1-5)\times10^{-3}$ M, and wavelength 350 nm. From the intercept and the slope of the straight line, ε_1 and K_1 are obtained. Since the concentration of free Cl^- ion, $[Cl^-]$, was not known at first, the total concentration of Cl^- ion, [Cl], was used instead and the successive approximation yielded the final values of ε_1 and K_1. An example of the linearity of Eq. (4) is shown in Fig. 3 and the values of K_1 at various x_M are listed in Table 1. The values of K_1 are recognized to grow larger as the concentration of methanol becomes higher, as is expected from a viewpoint of the dielectric constants of mixed solvents.

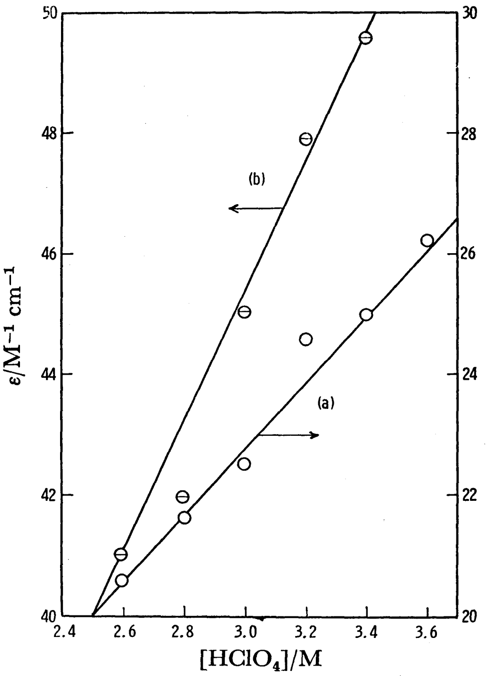

Fig. 2. Linear relationship between ε and $[HClO_4]$ at 25 °C and 350 nm. (a) $[Fe(III)] = 2.0\times10^{-2}$ M, $x_M = 0.2$; (b) $[Fe(III)] = 1.0\times10^{-2}$ M, $x_M = 0.935$.

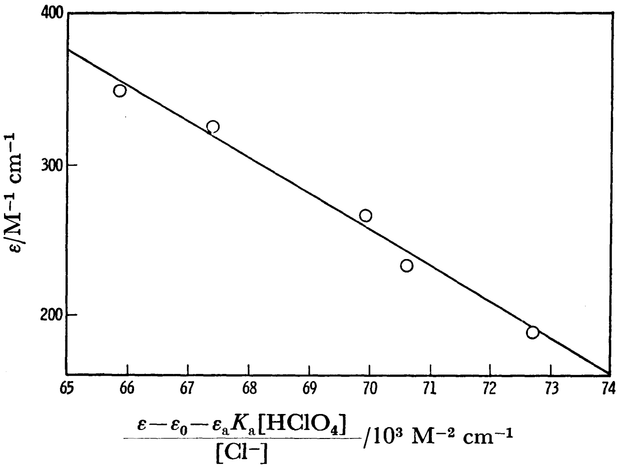

Fig. 3. Linear relationship between ε and $(\varepsilon-\varepsilon_0-\varepsilon_a K_a[HClO_4])/[Cl^-]$ at $[Fe(III)] = 2\times10^{-3}$ M, $[HClO_4]$ 3.0 M, $x_M = 0.20$, 25 °C, and 350 nm.

Rate Measurements. In the wavelength range of 300—400 nm, $FeCl^{2+}$ species exhibits an absorption peak at 350 nm, while species other than $FeCl^{2+}$ absorb light very little as compared to $FeCl^{2+}$. Therefore, the observations of the rate constants, k, were carried out at this wavelength; the observed transmittance of the reaction solution decreased as the reaction proceeded. The initial concentrations of the dissolved species were as follows: $[Fe(III)]=(1.5—2.0)\times 10^{-2}$ M, $[NaCl]=(1.5—2.0)\times 10^{-2}$ M, and $[HClO_4]=(1.25—8.00)\times 10^{-1}$ M. The occurrence of $FeCl_2^+$ and higher complexes was negligible.

Although the acid concentration is pretty high under the present circumstances, the $Fe(OH)^{2+}$ as a reactant and the $Fe(OH)Cl^+$ as a product must be taken into account in addition to Fe^{3+} and $FeCl^{2+}$ respectively. Then the following quantities are defined, the suffix e standing for the quantity at infinite time, namely at equilibrium:

$$[Fe] = [Fe^{3+}] + [FeOH^{2+}]$$

$$[FeCl] = [FeCl^{2+}] + [Fe(OH)Cl^{+}]$$

$$Q_1 = \frac{[FeCl]_e}{[Fe]_e[Cl^-]_e}$$

And the apparent reaction rate may be expressed by

$$\frac{d[FeCl]}{dt} = k[Fe][Cl^-] - k'[FeCl] \qquad (5)$$

where k and k' are the apparent forward and backward rate constants respectively. Since $Q_1=k/k'$ and $[Cl^-]=[FeCl]_e+[Cl^-]_e-[FeCl]$ and since [Fe] is approximately equal to $[Fe]_e$ at a later reaction time close to equilibrium, the following rate equation may be obtained:

$$\frac{d[FeCl]}{dt} = k\left\{[Fe]_e+\frac{1}{Q_1}\right\}\{[FeCl]_e-[FeCl]\} \qquad (6)$$

By integrating Eq. (6), the following correlation may be established:

$$-\ln\frac{[FeCl]_e-[FeCl]}{[FeCl]_e-[FeCl]_0} = k\left\{[Fe]_e+\frac{1}{Q_1}\right\}t \qquad (7)$$

The suffix 0 indicates the quantity at zero time of integration, but not at the true initial time of the reaction, because the stopped-flow apparatus does not record the initial quantity but begins to record some time after the initiation of the reaction. The quantity $([FeCl]_e-[FeCl])/([FeCl]_e-[FeCl]_0)$ is equal to $(A_e-A)/(A_e-A_0)$, which is easily obtained from the observations. The value of Q_1 is considered to be approximately equal to K_1. Examples of the linear relationships of Eq. (7) are drawn in Fig. 4 at $x_M=0.25$. From the linearities are obtained the apparent rate constants, k.

Acid Dependence of k. When the values of k at different acid concentrations at a constant x_M and temperature are plotted against $[H^+]^{-1}$, a straight line is obtained, as shown in Fig. 5. Taking this fact into account, the following reaction scheme is available:

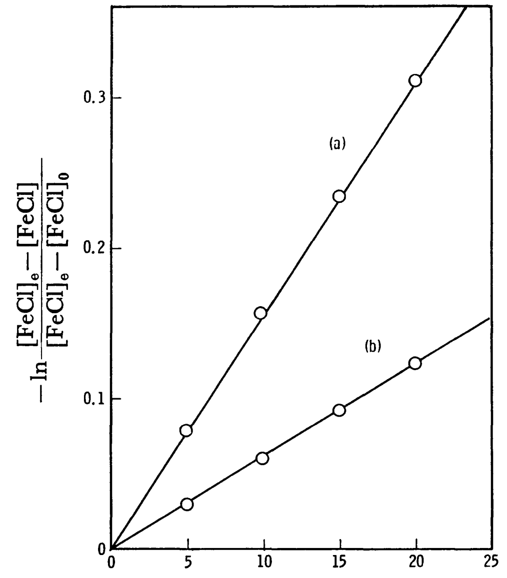

Fig. 4. Linear relationship between $-\ln([FeCl]_e-[FeCl])/([FeCl]_e-[FeCl]_0)$ and t at $F[e(III)]=[NaCl]=0.015$ M, $\mu=1.0$ M, $x_M=0.25$, and 350 nm. (a) $[HClO_4]=0.5$ M, 25.2 °C; (b) $[HClO_4]=0.8$ M, 22.5 °C.

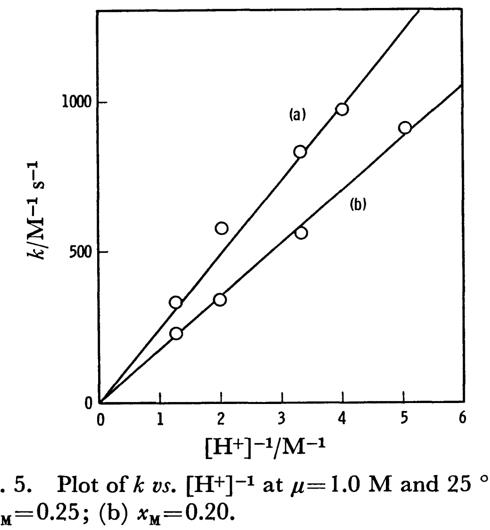

Fig. 5. Plot of k *vs.* $[H^+]^{-1}$ at $\mu=1.0$ M and 25 °C. (a) $x_M=0.25$; (b) $x_M=0.20$.

$$\begin{tikzcd} Fe^{3+} + Cl^- \arrow[r, shift left, "k_1"] \arrow[d, shift left, "-H^+"] & FeCl^{2+} \arrow[l, shift left, "k_1'"] \arrow[d, shift left, "-H^+"] \\ Fe(OH)^{2+} + Cl^- \arrow[r, shift left, "k_H"] \arrow[u, shift left, "H^+"] & Fe(OH)Cl^{+} \arrow[l, shift left, "k_H'"] \arrow[u, shift left, "H^+"] \end{tikzcd} \qquad (8)$$

Therefore, k is represented by

$$k = \frac{k_1+k_HK_H/[H^+]}{1+K_H/[H^+]} \qquad (9)$$

on the assumption that the rates of protonation and deprotonation are much larger than those of the ligand substitution under consideration. When the acid concentration is high enough, the denominator of Eq. (9) can be regarded as nearly equal to unity and thus the linear relationship between k and $[H^+]^{-1}$ in Fig. 5 becomes clear.

Table 2. Rate constants at 25 °C and activation parameters at different methanol concentrations

x_M	D^{-1}	k_1 $M^{-1}s^{-1}$	k_1' s^{-1}	k_H $M^{-1}s^{-1}$	$\Delta H_H^{\neq}+\Delta H_H^{\circ}$ kcal·mol^{-1}	$\Delta S_H^{\neq}+\Delta S_H^{\circ}$ cal·K^{-1}mol^{-1}	$\Delta G_{el}^{\neq}$ kcal·mol^{-1}	$\Delta G_0^{\neq}$ kcal·mol^{-1}
0	1.26×10^{-2}	7	2	1.2×10^{4}	19	13	−1.59	13.6
0.15	1.46×10^{-2}	9	0.4	2.6×10^{4}	20	18	−1.85	13.5
0.20	1.54×10^{-2}	2	0.05	2.8×10^{4}	21	22	−1.95	13.5
0.25	1.64×10^{-2}	6	0.1	2.8×10^{4}	—	—	−2.07	13.6
0.395	1.92×10^{-2}	21	0.2	6.3×10^{4}	24	34	−2.42	13.6
0.443	2.02×10^{-2}	30	0.2	7.6×10^{4}	—	—	−2.55	13.5
0.519	2.14×10^{-2}	30	0.3	1.00×10^{5}	23	33	−2.70	13.5

From the intercepts and the slopes of the straight lines expressed by Eq. (9), k_1 and k_H are calculated; these are listed in Table 2, along with the reverse rate constant k_1' calculated from $k_1/k_1'=K_1$. The values of k_1 and k_H in pure water agree well with those in the literature.[2] Although k_1 and k_1' are subjected to experimental errors to some extent, they still exhibit the trend that k_1 grows larger at higher x_M, while k_1' remains almost constant throughout the whole x_M range investigated. On the other hand, k_H is obtained more accurately than k_1, showing that k_H is approximately 10^3 larger than k_1 and that the higher the x_M, the larger the k_H value.

If we represent the hydrolysis equilibrium constant between the products in Scheme 8 as $K_{1H}=[Fe(OH)Cl^+][H^+]/[FeCl^{2+}]$, the following relation is given:

$$\frac{k_H}{k_H'}=\frac{K_{1H}}{K_H}\cdot\frac{k_1}{k_1'} \tag{10}$$

Since K_{1H} is supposed to be smaller than K_H on the basis of their electric charges, $(k_H/k_1)<(k_H'/k_1')$ is deduced, indicating that the hydrolyzed species is more favored in the backward reaction than in the forward.

Activation Parameters. A fact that both k_1 and k_H increase as x_M increases or the dielectric constant, D, of the mixed solvent decreases is consistent with an electrostatic expectation. According to Amis' equation,[4]

$$\ln k_H=\ln k_H^{\circ}-\frac{Z_A Z_B e^2}{kTrD} \tag{11}$$

ln k_H should show a linear relationship with respect to D^{-1} at constant temperature, where Z_A and Z_B stand for the numbers of electric charges on $Fe(OH)^{2+}$ and Cl^- ions respectively, e is the elementary electric charge, r is the distance between the two ions in the activated state, k is Boltzmann's constant, and k_H° is a rate constant which implies a rate constant at infinite dielectric constant. Figure 6 represents the relationship of ln k_H *vs.* the reciprocal dielectric constant of the mixed solvent, with a fine linearity from whose slope $r=5.34$ Å is obtained.

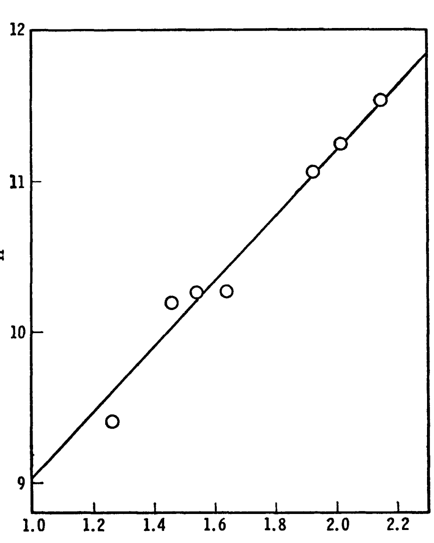

Fig. 6. Plot of ln k_H *vs.* D^{-1} at $\mu=1.0$ M and 25 °C.

When the values of radii $r(Fe^{3+})=0.67$ Å, and $r(Cl^-)=1.81$ Å, and of diameter $d(H_2O)=3.0$ Å are used, $r(Fe^{3+})+r(Cl^-)+d(H_2O)$ is equal to 5.5 Å, which is very close to the experimental result. Thus, the dimension of the activated complex is reasonable for a structure $[OH^--Fe^{3+}-H_2O-Cl^-]$ which supports the outer-sphere mechanism of the reaction, and also indicates that a probable mixed solvation of methanol molecules in the coordination sheath of the complex at rather high x_M is independent of the reaction rate. This may be a proof of the reaction mechanism not only for the Fe(III)–Cl^- system[1,5] but for other similar systems such as Fe(III)–N_3^- [6] and Fe(III)–SCN^-.[7]

Temperature dependence of $k_H K_H$ was measured; their Arrhenius plots against T^{-1} offer the activation parameters for the reaction in each solvent. Since the temperature dependence of K_H was not measured separately, $(\Delta H_H^{\neq}+\Delta H_H^{\circ})$ and $(\Delta S_H^{\neq}+\Delta S_H^{\circ})$ are the sum of the activated and the standard enthalpies and entropies for the reaction $Fe(OH)^{2+}+Cl^-\rightarrow Fe(OH)Cl^+$, respectively; the values are listed in Table 2. According to the values in Table 2, $(\Delta H_H^{\neq}+\Delta H_H^{\circ})$ exhibits a linear relationship with $(\Delta S_H^{\neq}+\Delta S_H^{\circ})$, as is

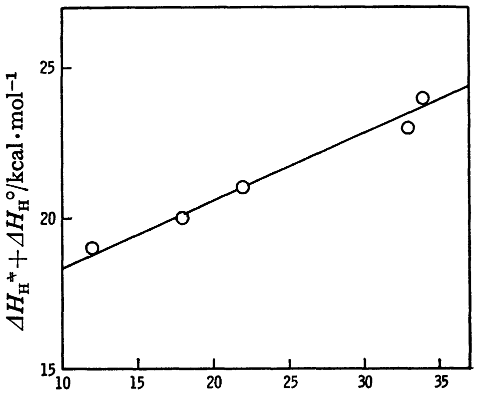

Fig. 7. Compensation relationship between $(\Delta H_H^{\neq}+\Delta H_H^{\circ})$ and $(\Delta S_H^{\neq}+\Delta S_H^{\circ})$.

shown in Fig. 7. This points out the occurrence of a compensation effect with an isokinetic temperature of 225 K, which is −48 °C.

The establishment of the linearity by Eq. (11) indicates that the free energy of activation $\Delta G_{\mathrm{H}}^{\neq}$ consists of the electric part $\Delta G_{\mathrm{el}}^{\neq}$ and the non-electrical one $\Delta G_{\mathrm{O}}^{\neq}$, the latter being indifferent to the composition of the solvent.

$$\Delta G_{\mathrm{H}}^{\neq} = \Delta G_{\mathrm{el}}^{\neq} + \Delta G_{\mathrm{o}}^{\neq} \qquad (12)$$

Since $\Delta G_{\mathrm{el}}^{\neq} = NZ_{\mathrm{A}}Z_{\mathrm{B}}e^2/rD$ according to Eq. (11) where N is Avogadro's number, and $\Delta G_{\mathrm{H}}^{\neq} = RT(\ln(kT/h) - \ln k_{\mathrm{H}})$, $\Delta G_{\mathrm{O}}^{\neq}$ is also easily calculated. The results of this calculation are shown in Table 2. As a matter of course, $\Delta G_{\mathrm{O}}^{\neq}$ is constant with a mean value of 13.5 kcal/mol. $\Delta G_{\mathrm{el}}^{\neq}$ is related to the free energy change due to the approach of the two reacting ions as close as the distance of the activated complex in the dielectric medium and $\Delta G_{\mathrm{O}}^{\neq}$ to that caused by the atomic and electronic configuration in the activated complex.

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